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Abstract

CORROSION IN AQUEOUS SYSTEMS

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The successful operation of water-cooled power reactors has established the good corrosion resistance and overall satisfactory performance of Zircaloy-2 and stainless steel as fuel element jacketing materials.

In some experiments, Zircaloy-2 has been shown to exhibit multiple transitions in corrosion rate in high temperature water; it is inferred that periodic breakdown in the protectiveness of the oxide occurs. After exposure in pressurized water reactors, boiling water reactors and in-reactor loops, Zircaloy-2 jacketing has sometimes shown no effect of reactor environment on corrosion; at others there has been a significant increase.

For water exposure at normal reactor temperatures, only the reduction in mechanical properties, as a consequence of hydrogen absorption, appears to be a potential limitation to the useful life of the alloy. If the temperature is increased above the range 400-450C, the oxide film loses its tenacity and the corrosion rate increases substantially. Thus, extrapolation of the use of Zircaloy to high temperature superheated steam applications does not seem feasible.

A modification of Zircaloy-2, designated Zircaloy-4, has retained the favorable properties of Zircaloy-2 and has reduced hydrogen pickup during water corrosion. Other zirconium alloys have improved resistance to corrosion by superheated steam. At temperatures as high as 650C hydrogen absorption is slight, but embrittlement due to oxygen pickup is potentially serious. Also, niobium alloys have been developed which have higher strength and equivalent resistance to water corrosion; in superheated steam, certain niobium alloys have lower corrosion rates than do zirconium alloys.

The corrosion rate of chromium-nickel stainless steels is low in water at temperatures of interest. In superheated steam corrosion rates of austenitic

steels increase markedly above 540C. Both from the point of view of penetration and of corrosion product formation, rates are probably unacceptably high for type 304 stainless steel at 650C. Certain chromium-bearing ferritic steels have shown substantially better corrosion resistance at this temperature than the austenitc steels. Some nickel-base alloys also exhibited the lower corrosion rates.

For stainless steels, the problem of major concern has been stress-corrosion cracking. It has been observed in heat exchangers; in superheated steam, where a number of experimental stainless steel jacketed fuel elements failed; in reactor water at a wide range of temperatures; in high temperature uranyl sulfate solution. The presence of chloride ion has generally been indicated to be necessary for cracking to occur. In low chloride environments, local concentration of the ion is observed as a result of evaporation with limited mixing, and of the ion exchange characteristics of deposited oxides. Certain of the nickel-base alloys seem immune to chloride-induced stress-corrosion cracking.

Susceptibility to stress-corrosion cracking has been related to the stress-induced formation of a parallel network of dislocations, and to the "mean atomic diameter" of metal atoms in nickel-chromium-iron alloys.

In nearly pure water, the corrosion of carbon steels and low alloy steels is accelerated by minor amounts of oxygen dissolved in the water. At higher oxygen contents, depending on temperature, protective films are formed and corrosion rates are again low.

In pressurized water systems, the pH is controlled in the alkaline range to minimize deposition on heat transfer surfaces of transported corrosion products. However, alkali metal hydroxide content increases at crevices where local boiling occurs and where alternate wetting and drying occur in steam phase areas. Such strong solutions can induce stress-corrosion cracking in carbon and stainless steels, and cause marked acceleration of the corrosion of Zircaloy-2 and low alloy steels. In the latter case, lithium hydroxide is less dangerous than the other alkalis, apparently because its concentration is prevented from reaching a harmful level by the formation of a mixed lithium iron oxide.

In aqueous systems, corrosion products are removed from the site of formation by dissolution as well as by physical removal of particles. The particulate material deposits at places of change in flow direction, in turbulent regions, on heated surfaces and in radioactive areas. Dissolved oxides do not generally deposit at such locations, but precipitate where the temperature is low.